

# Dynamic equivalence between atomic and colloidal liquids

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We show that the kinetic-theoretical self-diffusion coefficient of an atomic fluid plays the same role as the short-time self-diffusion coefficient  $D_S$  in a colloidal liquid, in the sense that the dynamic properties of the former, at times much longer than the mean free time, and properly scaled with  $D_S$ , will be indistinguishable from those of a colloidal liquid with the same interaction potential. One important consequence of such dynamic equivalence is that the ratio  $D_L/D_S$  of the long-time to the short-time self-diffusion coefficients must then be the same for both, an atomic and a colloidal system characterized by the same inter-particle interactions. This naturally extends to atomic fluids a well-known dynamic criterion for freezing of colloidal liquids [Phys. Rev. Lett. **70**, 1557 (1993)]. We corroborate these predictions by comparing molecular and Brownian dynamics simulations on the hard-sphere system and on other soft-sphere model systems, representative of the “hard-sphere” *dynamic* universality class.

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One of the fundamental challenges in understanding the relationship between dynamic arrest phenomena in colloidal systems [1], and the glass transition in simple glass-forming atomic liquids [2], is to determine the role played by the underlying (Brownian vs. Newtonian) microscopic dynamics. It is a widespread notion that colloidal systems constitute a mesoscopic analog of atomic systems regarding the relationship between inter-particle forces and macroscopic properties [3, 4]. The molecular dynamics simulation of an atomic liquid, for example, is expected to yield the same equilibrium phase diagram, and a similar dynamic arrest scenario, as the Brownian dynamics simulation of a colloidal liquid, when referring to the same model system [5, 6]. Important questions, however, remain unanswered, even at normal liquid states, far from the neighborhood of the conditions for dynamic arrest. For example, while it is well-known that monodisperse Brownian liquids will freeze when the long-time self-diffusion coefficient  $D_L$  reaches about  $0.1 \times D_S$ , with  $D_S$  being the short-time self-diffusion coefficient (“Löwen’s dynamic freezing criterion” [7]), no analogous criterion has been identified for the corresponding atomic liquids.

In the attempt to develop the extension to *atomic* liquids, of the self-consistent generalized Langevin equation (SCGLE) theory of *colloid* dynamics [8], we have discovered that a well-defined long-time dynamic equivalence between atomic and colloidal liquids emerges upon the identification of the kinetic-theoretical self-diffusion co-

efficient  $D^0$  of an atomic fluid [9], as the analog of the short-time self-diffusion coefficient  $D_S$  of a colloidal liquid. In this short communication we describe the physical foundations of this extended SCGLE theory, which also constitute the physical basis of the referred dynamic equivalence. One of the most important manifestations of the latter is that the ratio  $D^* \equiv D_L/D_S$  must then be the same for an atomic and a colloidal system characterized by the same inter-particle interactions, thus naturally extending Löwen’s freezing criterion to atomic systems. To corroborate these predictions we generate and compare molecular and Brownian dynamics simulations on hard- and soft-sphere model systems representative of the class of systems whose long-time dynamics maps onto the dynamics of the hard-sphere fluid, i.e., that pertain to the “hard-sphere” *dynamic* universality class [10].

Let us start by considering a model atomic fluid, formed by  $N$  spherical particles of mass  $M$  in a volume  $V$ , interacting through the pair potential  $u(r)$ , whose microscopic dynamics is described by Newton’s equations. The fundamental concept upon which we construct our theory for these properties is the role of the mean free time,  $\tau_0$ , defined in the kinetic theory of gases as the characteristic timescale that provides the crossover from the short-time ballistic motion of the atoms to their long-time diffusive transport. It is well known that for correlation times  $t$  much shorter than  $\tau_0$ , and for distances much shorter than the mean free path  $l_0$ , all the particles move ballistically. For times  $t$  much longer than  $\tau_0$ , each parti-

cle has undergone many collisions, and its motion can be represented as a sequence of random (ballistic) flights of mean length  $l_0 \sim 1/(n\sigma^2)$ . As a consequence, for  $t \gg \tau_0$  each individual particle moves diffusively, with a diffusion coefficient given by [11]  $D^0 = (l_0)^2/\tau_0 = l_0 v_0 \sim \sqrt{k_B T/M}/(n\sigma^2)$  (where  $l_0/\tau_0 = v_0 \equiv (k_B T/M)^{1/2}$  is the thermal velocity). In fact, the rigorous value of  $D^0$ , determined by the kinetic theory of gases [9], is

$$D^0 \equiv \frac{3}{8\sqrt{\pi}} \left( \frac{k_B T}{M} \right)^{1/2} \frac{1}{n\sigma^2}. \quad (1)$$

This immediately implies that, on the average, the motion of each individual particle crosses over from ballistic to diffusive, at the crossover timescale  $\tau_0$ , and that this crossover behavior must be described by the ordinary Langevin equation [11, 12] for the instantaneous velocity  $\mathbf{v}(t)$  of a representative tracer particle,  $M d\mathbf{v}(t)/dt = -\zeta^0 \mathbf{v}(t) + \mathbf{f}^0(t)$ . In this equation, the friction coefficient  $\zeta^0$  is defined by Einstein's relation,  $\zeta^0 \equiv k_B T/D^0$ , with  $D^0$  given by the kinetic-theoretical result in Eq. (1) above. This strongly suggests a deeper analogy between the dynamics of Newtonian and Brownian liquids, and hence, some form of dynamic equivalence between atomic and colloidal dynamics, at least regarding tracer diffusion phenomena. Thus, in both cases the relaxation time  $\tau_0 = [M/\zeta^0]$  of the velocity, due to the friction force  $-\zeta^0 \mathbf{v}(t)$ , defines the crossover from ballistic ( $t \ll \tau_0$ ) to diffusive ( $t \gg \tau_0$ ) motion.

The fundamental difference lies, of course, in the physical origin of the friction force  $-\zeta^0 \mathbf{v}(t)$  and in the definition of the friction coefficient  $\zeta^0$ . In a colloidal liquid this friction is caused by an “external” material agent, namely, the supporting solvent, which also acts as a heat reservoir. In an atomic liquid, in contrast, the friction force  $-\zeta^0 \mathbf{v}(t)$  is not caused by any external agent, but by the spontaneous tendency to establish, or restore, through molecular collisions, the equipartition of the energy available for distribution among the kinetic energy degrees of freedom of the system. Thus, in this case the friction force  $-\zeta^0 \mathbf{v}(t)$  is the dissipative response of the system towards the restoration of this partial thermal equilibrium through collisional heat transport, and the spontaneous fluctuations around this equipartition is the source of the fluctuating force  $\mathbf{f}^0(t)$ . As a consequence, the corresponding value of  $\zeta^0$  is determined by the kinetic-theoretical result for  $D^0$  in Eq. (1), through Einstein's relation  $\zeta^0 \equiv k_B T/D^0$ .

The friction and fluctuating terms of the *atomic* Langevin equation are, of course, a consequence of the interatomic collisions of the tracer particle with the rest of the particles in the fluid, an effect that could also be described by the *kinetic* terms of the pressure tensor  $\overset{\leftrightarrow}{\Pi}(\mathbf{r}, t)$  of the fluid formed by the surrounding particles. The *configurational* components of  $\overset{\leftrightarrow}{\Pi}(\mathbf{r}, t)$ , on the other hand, correspond to the usual direct force

$-\nabla_T \sum_{i=1}^N u(\mathbf{r}_{iT})$  (where “T” stands for “tracer”). This force, whose effects must still be taken into account, can also be written exactly as  $\int d^3r [\nabla u(\mathbf{r})] n(\mathbf{r}, t)$ , where  $n(\mathbf{r}, t)$  is the local density of particles at position  $\mathbf{r}$  referred to the tracer particle's center [13]. Thus, from the superposition of forces, the complete Langevin equation for a tracer particle in an atomic liquid actually reads  $M d\mathbf{v}(t)/dt = -\zeta^0 \mathbf{v}(t) + \mathbf{f}^0(t) + \int d^3r [\nabla u(\mathbf{r})] n(\mathbf{r}, t)$  [14]. By writing the time-evolution equation of  $n(\mathbf{r}, t)$  (linearized around equilibrium), and by substituting the solution in this configurational contribution of the direct interactions, one can transform [13] this direct force term, into another friction term plus its corresponding fluctuating force, namely,

$$M \frac{d\mathbf{v}(t)}{dt} = -\zeta^0 \mathbf{v}(t) + \mathbf{f}^0(t) - \int_0^t dt' \Delta\zeta(t-t') \mathbf{v}(t') + \mathbf{F}(t). \quad (2)$$

In this equation the term involving the time-dependent friction function  $\Delta\zeta(t)$  describes the mean dissipative friction effects due to the collective direct force on the tracer particle, whose random component is the Gaussian stationary stochastic force  $\mathbf{F}(t)$ . The derivation of this equation follows step by step the derivation originally carried out for colloidal liquids [13]; it is now explained in detail for atomic fluids in Ref. [15]. One of the main products of such derivation is the following approximate but general expression for  $\Delta\zeta^*(t) \equiv \Delta\zeta(t)/\zeta^0$ , in terms of the static structure factor  $S(k)$  and of the *collective* and *self* intermediate scattering functions (ISF)  $F(k, t)$ , and  $F_S(k, t)$  [3] of the fluid surrounding the tracer particle,

$$\Delta\zeta^*(t) = \frac{D_0}{3(2\pi)^3 n} \int d\mathbf{k} \left[ \frac{k[S(k) - 1]}{S(k)} \right]^2 F(k, t) F_S(k, t), \quad (3)$$

which is then also applicable in the present atomic case.

In order to evaluate  $\Delta\zeta^*(t)$  we thus need to determine  $F(k, t)$  and  $F_S(k, t)$  at least in the diffusive regime  $t \gg \tau^0$ , since the effects described by  $\Delta\zeta^*(t)$  in Eq. (2) only manifest themselves at times longer than the crossover time  $\tau^0$ . For this, one can employ the generalized Langevin equation formalism [13] to derive the general memory function expressions for the ISFs of an atomic liquid. Such an exercise is described in Ref. [16]. As a result one derives general expressions for  $F(k, t)$  and  $F_S(k, t)$ , which in principle describe the dynamics of the atomic liquid in the full time-domain, from the ballistic to the diffusive regimes. Requesting consistency of such general expressions, with the physical picture leading to Eq. (2) above, these expressions for  $F(k, t)$  and  $F_S(k, t)$  can be written in the long-time (or “over-damped”) limit in terms of the corresponding memory functions,  $C(k, t)$  and  $C_S(k, t)$ . The latter may then be approximated, as suggested in Ref. [8], by  $C(k, t) = C_S(k, t) = \lambda(k) \Delta\zeta^*(t)$ , so that the resulting long-time expressions for  $F(k, t)$  and  $F_S(k, t)$  can finally be written,

in Laplace space, as [16]

$$F_S(k, z) = \frac{1}{z + \frac{k^2 D^0}{1 + \lambda(k) \Delta \zeta^*(z)}} \quad (4)$$

and

$$F(k, z) = \frac{S(k)}{z + \frac{k^2 D^0 S^{-1}(k)}{1 + \lambda(k) \Delta \zeta^*(z)}}, \quad (5)$$

where the function  $\lambda(k)$  is given by  $\lambda(k) = 1/[1 + (k/k_c)^2]$ , with  $k_c = 1.35(2\pi/\sigma)$ .

For a given static structure factor  $S(k)$ , Eqs. (3)-(5) constitute a closed system of equations, which turns out to be identical to the equations that summarize the self-consistent generalized Langevin equation (SCGLE) theory of *colloid* dynamics [8]. Thus, these equations, which constitute an “atomic” extension of the SCGLE theory, predict that the long-time dynamic properties of an atomic liquid will then coincide with the corresponding properties of a colloidal system with the same  $S(k)$ , provided that the time is scaled as  $D^0 t$  and that the respective meaning and definition of  $D^0$  is taken into account (i.e., that  $D^0$  is given either by the short-time self-diffusion coefficient in the case of the colloidal liquid, or by Eq. (1) in the case of the atomic fluid). One obvious example of such long-time properties is the long-time self-diffusion coefficient  $D_L \equiv \lim_{t \rightarrow \infty} \langle (\Delta \mathbf{r}(t))^2 \rangle / 6t$ , whose value for an atomic system, scaled as  $D^* \equiv D_L/D^0$ , is thus predicted to be indistinguishable from the corresponding property of the equivalent colloidal system.

This is an important and distinct prediction of the SCGLE theory, whose accuracy can be readily checked without even solving the corresponding self-consistent approximate equations above, since one can compare molecular and Brownian dynamics results for the long-time self-diffusion coefficient of a given specific system. Thus, in Fig. 1 we plot molecular dynamics data for  $D_L(\phi)$  of a hard-sphere fluid both, in the “usual” atomic units  $\sigma(k_B T/M)^{1/2}$ , and scaled as  $D^*(\phi) \equiv D_L(\phi)/D^0(\phi)$ , with  $D^0(\phi)$  given by Eq. (1). The same figure also presents available Brownian dynamics simulation results for  $D_L(\phi)$  of the hard sphere system without hydrodynamic interactions, scaled as  $D^*(\phi) \equiv D_L(\phi)/D^0$ , with  $D^0$  being the  $\phi$ -independent short-time self-diffusion coefficient of the Brownian particles. Clearly, the “colloidal” and the “atomic” results for  $D^*$  collapse onto the same curve, which we denote by  $D_{HS}^*(\phi)$ . One immediate and important consequence of this comparison is the extension to atomic liquids of Löwen’s dynamic criterion for freezing: now for both, the atomic and the colloidal HS fluids, the condition  $D_{HS}^*(\phi) \approx 0.1$  occurs at  $\phi = \phi_{HS}^{(f)} = 0.494$ .

This long-time colloidal–atomic correspondence is also observed in the  $\alpha$ -relaxation time  $\tau_\alpha(k; \phi)$ , defined by the condition  $F_S(k, \tau_\alpha) = 1/e$ , but only in the metastable

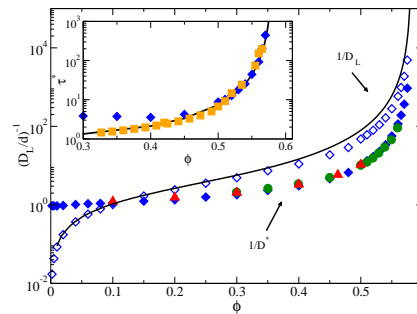


FIG. 1: Long-time self-diffusion coefficient  $D_L(\phi)$  (main figure), and dimensionless  $\alpha$ -relaxation time  $\tau^*(k) \equiv k^2 D^0(\phi) \tau_\alpha(k; \phi)$  at  $k\sigma = 7.1$  (inset), of the hard-sphere fluid. The results of the molecular dynamics simulations described in Ref. [17] for  $D_L(\phi)$  are expressed in “atomic units” (i.e., with  $d = \sigma(k_B T/M)^{1/2}$ , empty diamonds), and scaled as  $D^*(\phi) \equiv D_L(\phi)/D^0(\phi)$ , with  $D^0(\phi)$  given by Eq. (1) (i.e.,  $d = D^0(\phi)$ , full diamonds). The corresponding results for  $\tau^*(k)$  are the full diamonds in the inset. The other full symbols are the *Brownian* dynamics simulation results for  $D^*$  from Refs. [18] (triangles) and [19] (circles), and for  $\tau^*$  from our present BD simulation results for HS using the method described in Ref. [20] (squares). The solid lines correspond to the solution of the SCGLE theory.

liquid regime. This is illustrated in the inset of Fig. 1, which demonstrates that the molecular dynamics and the Brownian dynamics data for  $\tau^*(k) \equiv k^2 D^0 \tau_\alpha(k; \phi)$  evaluated at  $k\sigma = 7.1$  collapse onto a common curve in the metastable fluid regime,  $0.5 \lesssim \phi$ , but for  $\phi$  below freezing, both data depart from each other. The reason for this is that in reality, for  $\phi \lesssim 0.5$ , the dynamics of  $F_S(k, t)$  at times  $t \approx \tau_\alpha$  is not yet described by the long-time asymptotic expressions in Eqs. (4) and (5); instead,  $F_S(k, t)$  is closer to its ballistic approximation  $F_S(k, t) \approx \exp[-k^2 v_0^2 t^2 / 2]$ , so that  $\tau_\alpha(k; \phi) \approx \sqrt{2}/k v_0$  (for colloidal fluids,  $\tau_\alpha(k; \phi) \approx 1/k^2 D^0$  at low densities).

Let us also point out that besides comparing MD vs. BD simulation data, one can, of course, also solve Eqs.(3), (4), and (5) to actually calculate theoretically  $D_{HS}^*(\phi)$  and  $\tau^*(k)$ . The solid lines in Fig. 1 are the result of such numerical calculation, with  $S(k)$  provided by the Percus-Yevick approximation [21] with its Verlet-Weis correction [22]. In fact, let us mention that the data for  $\tau^*(k)$  in the inset were employed to calibrate the parameter  $k_c$  in the function  $\lambda(k)$ , thus leading to the quoted value  $k_c = 1.35(2\pi/\sigma)$ .

Another manner to express this long-time dynamic universality of atomic and colloidal liquids is to plot the simulated data of the dimensionless MSD  $w(t^*) \equiv \langle (\Delta \mathbf{r}(t))^2 \rangle / 6l_0^2$  as a function of the dimensionless time  $t^* \equiv t/\tau_0$ . From the generalized Langevin equation (GLE) in Eq. (2) one can derive the following equation

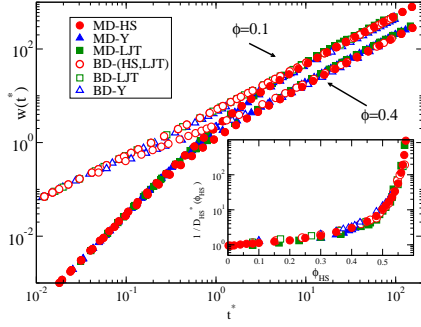


FIG. 2: Main figure: Scaled mean squared displacement  $w(t^*) \equiv \langle (\Delta \mathbf{r}(t))^2 \rangle / 6l_0^2$  as a function of the dimensionless time  $t^* \equiv t/\tau_0$ , simulated with molecular dynamics (MD, solid symbols) and Brownian dynamics (BD, empty symbols) for fluids with hard-sphere (HS, circles), truncated Lennard-Jones (TLJ, squares) and repulsive Yukawa (Y, triangles) interactions, for states corresponding to  $\phi_{HS} = 0.1$  and  $0.4$ . Inset: simulation data for the scaled long-time self-diffusion coefficient  $D^*$  of the same systems (and same symbols), plotted as a function of the effective HS volume fraction  $\phi_{HS} = \phi_{HS}(n, T)$ .

for  $w(t^*)$

$$\frac{dw(t^*)}{dt^*} + w(t^*) = t^* - \tau^0 \int_0^{t^*} \Delta \zeta^*(t^* - t'^*) w(t'^*) dt'^*, \quad (6)$$

whose solution satisfies the short- and long-time limits  $w(t^* \rightarrow 0) \approx t^{*2}/2$  and  $w(t^* \rightarrow \infty) \approx D^* t^*$ , with  $D^* = 1/[1 + \Delta \zeta^*(z = 0)]$ . This scaling, however, hides the true timescales for atomic and colloidal systems, which differ by many orders of magnitude [15]. For example, the cross-over time  $\tau_0$  from ballistic to diffusive motion is of the order of one picosecond in an atomic liquid and of tens of nanoseconds in a typical colloidal system, whereas the crossover time from short to long time diffusion,  $\tau_I \equiv d^2/D^0$  (with  $d = n^{-1/3}$ ), is of the order of tens of picoseconds in an atomic liquid and of a fraction of a second in a colloidal liquid. Thus, in a colloidal fluid  $\tau_I \approx 10^7 \tau_0$ , and hence, the ballistic short-time regime is generally unimportant. Thus, one normally redefines “short times” by first taking the “overdamped” limit (i.e., dropping the inertial term in Eqs. (2) and (6)). This only changes the short-time limit to  $w(t^*) \approx t^*$ , but leaves unaltered the long-time limit  $w(t^*) \approx D^* t^*$ . Thus, except for these short-time differences, the msd of an atomic and a colloidal liquid with the same interactions and the same  $S(k)$  should be indistinguishable at long times. This is precisely what is illustrated in Fig. 2, which plots the simulated data of  $w(t^*)$  as a function of  $t^*$  for the hard-sphere system at two volume fractions,  $\phi = 0.1$  and  $0.4$ .

Fig. 2 also illustrates the fact that this colloidal–atomic dynamic correspondence is not restricted to the hard-sphere fluid, but it actually extends over to systems

with soft repulsive interactions. This is a direct result of combining the present colloidal–atomic correspondence for the hard sphere system, with another important scaling rule, which derives from the principle of dynamic equivalence between soft-sphere and hard-sphere liquids [10]. This principle states that the dynamic properties of a colloidal liquid at number concentration  $n$  and temperature  $T$ , whose particles interact through a repulsive soft-sphere pair potential  $u(r)$ , will be given by those of the hard-sphere system with an effective hard-sphere volume fraction  $\phi_{HS}(n, T)$  determined by the iso-structurality condition,  $S(k_{mak}; n, T) = S_{HS}(k_{mak}^{(HS)}; \phi_{HS})$ , which requests that the height of the main peak of the static structure factor of the “real” soft-sphere system, and of the effective hard-sphere system, coincide. As a consequence one has, for example, that the msd scales as  $w(t^*; n, T) = w_{HS}(t^*; \phi_{HS}(n, T))$  and that the curve  $D_{HS}^*(\phi)$  in Fig. 1 becomes a universal curve for all colloidal soft-sphere liquids, provided that its horizontal axis refers to the effective volume fraction  $\phi_{HS}(n, T)$ .

The extension of this scaling to atomic systems is immediate once the collision diameter  $\sigma$  entering in the expression for  $D^0(n, T)$  in Eq. (1) is given a proper definition for the soft-sphere potential  $u(r)$  considered. We found that replacing this collision diameter by  $\sigma_{HS}(n, T) \equiv [6\phi_{HS}(n, T)/\pi n]^{1/3}$  seems to be a simple and reasonably universal approximation. To assess the accuracy of the resulting general scaling, we generated molecular and Brownian dynamics simulation data for the truncated Lennard-Jones system,  $u(r)/k_B T = T^{*-1}[(\sigma/r)^{12} - 2(\sigma/r)^6 + 1]\theta(\sigma - r)$ , at fixed reduced temperature  $T^* = 1$ , and for the repulsive Yukawa potential  $u(r)/k_B T = K \exp[-z(r/\sigma - 1)]/(r/\sigma)$ , with  $K = 554$  and  $z = 0.149$ . In both cases, the densities were chosen to correspond to effective HS systems at volume fractions  $\phi_{HS}(n, T) = 0.1$  and  $0.4$ . The results for  $w(t^*; n, T)$  in Fig. 2 illustrate that, plotted in this scaled manner, the long-time limit of  $w(t^*; n, T)$  will not discriminate between atomic or colloidal systems and between soft- and hard-sphere interactions. Thus, from any of these simulations one should be able to determine  $D^*$ . To illustrate this, in the inset of Fig. 2 we plot the simulated data of  $D^*(n, T)$  for these two soft-sphere model systems as a function of  $\phi_{HS}(n, T)$ , which clearly collapse onto the curve  $D_{HS}^*(\phi_{HS})$ , represented in the figure by the HS MD data.

In summary, we have shown that at least for model liquids whose structure is dominated by (soft- or hard-sphere) repulsive interactions, the long-time dynamics of atomic liquids is indistinguishable from the dynamics of the colloidal systems with the same inter-particle interactions. As a consequence, just like the equilibrium thermodynamic and structural properties, some dimensionless long-time dynamic properties, such as  $D^*$  and  $\tau^*(k)$  (the latter only in the supercooled liquid regime), will exhibit the same independence from the short-time mi-

croscopic dynamics which otherwise distinguishes atomic from colloidal systems. It is reasonable to expect that this dynamic universality will be useful in understanding, for example, the relationship between dynamic arrest phenomena in colloidal systems, and the glass transition in simple glass-forming atomic liquids.

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